PS09.01.12 4f-ELECTRON DENSITY DISTRIBUTION IN CeB$_6$ AND ITS TEMPERATURE DEPENDENCE.

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The electron density in CeB$_6$ was measured at 100K, 165K, 230K and 298K and the large peaks on the deformation density map near Ce were first confirmed to be those of 4f-electrons by the X-ray Atomic Orbital Analysis. The results at the four temperatures will be also compared to reveal the origin of the Kondo effect of CeB$_6$.

Rare-earth elements have been widely used in industries and they are also involved in high-temperature super conductors. However the measurement of the f-electron density has been judged to be difficult mainly because of the much severer systematic errors such as absorption, extinction and multiple difffraction(MD) of compounds with heavy atoms. Recently we have demonstrated that the MD could not be neglected in accurate structure factor measurements of crystals with heavy atoms and started the measurement avoiding the MD. The structure factors thus measured at 165K and 100K revealed the large peaks along <100> around Ce. They were analyzed based on the crystal field model utilizing the scattering factors calculated with the relativistic atomic orbitals and confirmed to be those of T1u 4f-orbitals in the Oh crystal field. The deformation density around B corresponds very well to the calculated molecular orbitals of the B$_6$ molecule and that of CaB$_6$ composed only of the light atoms, which guarantee the accuracy of the present experiment.

PS09.01.13 ELECTRON DENSITY STUDIES OF METAL SQUARATE COMPLEXES.

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Metal squarate complexes, $M(C_4O_4)(H_2O)_4$, (M = Fe, Co, Ni, Zn), are known to have a polymeric chain structure with $C_4O_4^{2-}$ served as a bridge (μ-2) ligand, between two metal ions at transposition. Each metal ion is bonded to two $C_4O_4^{2-}$ and four water molecules. They are all isostructural with space group C2/c. A complete Ewald sphere of data is measured up to 2θ of 100° by using Mo Kα radiation at 110K for Fe and Zn complexes and 130K for Ni and Co complexes. Such carefully measured intensities are used to investigate the detail electron density distribution in order to understand the chemical bonding and the d-orbital splitting subjected in the ligand field. Results on the electron density distribution will be presented in the form of deformation density maps, where indepent isolated spherical atom are substracted from the molecular electron density. Deformation density will be presented in term of $\Delta\rho_{x-x}$, $\Delta\rho_{m-a}$ (multipole model) and $\Delta\rho$ calculated from the MO calculation. The interesting bent-bond feature on the four-membered-ring ligand $C_4O_4^{2-}$can be easily illustrated by the deformation density distributions. The asphericity in electron density distribution around the metal ion is also clearly demonstrated. The comparison on this series of 3d-transition metal complexes will be presented in terms of d-orbital populations and the deformation density distribution. The total number of d-electrons from the experiments are 6.02, 6.82, 7.81, 8.56 respectively for Fe(II), Co(II), Ni(II), Zn(II) ions in these compounds.

PS09.01.14 X-N STUDY OF THE ELECTRON DENSITY DISTRIBUTION IN Ni(ND$_3$)$_4$(NO$_2$)$_2$ AT 9 K.

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The electron density distribution (ED) of Ni(ND$_3$)$_4$(NO$_2$)$_2$ has been determined from 9 K AgKα X-ray diffraction data in combination with 13 K Time-of-flight (TOF) neutron diffraction data. Excellent agreement is obtained between positional and thermal parameters derived separately from the two experiments. This demonstrates that, also for complex systems, TOF neutron diffraction can produce structural parameters of a quality comparable to measurements with monochromatic neutrons. The valence orbital model used to model the ED in a previous study of Ni(ND$_3$)$_4$(NO$_2$)$_2$ (1) turned out to be inadequate for describing the more accurate very low-temperature data which extend to sinθ/λ= 1.4 Å^{-1}. Instead a multipole model with extra radial flexibility is used to obtain a satisfactory description of the data. The bonding in Ni(ND$_3$)$_4$(NO$_2$)$_2$ is discussed based on representations of the total ED. Topological analysis of the static model density is used to describe the metal-ligand interactions. Both ligands are bonded to Ni through closed shell interactions, but the ellipticity in the Ni-nitro bond is larger than in the Ni-ammine bond. This suggests larger pi-type contributions to the Ni-nitro bond than to the Ni-ammine bond.

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PS09.01.15 CHARGE AND SPIN DENSITY IN SOME HYDRATES OF NICKEL SALTS: BONDING AND ARTIFICIAL EFFECTS.

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There appears to be conflicting experimental evidence on the redistribution of the charge density in the lone-pair and other regions of a molecule due to the interaction with its nearest neighbours. In some experimental as well as theoretical deformation density maps a decrease in the lone-pair density has been reported, whereas in other cases an increase has been found. It appears that two major, counteracting factors are responsible for these differences: an increase in the lone-pair density is expected due to the polarizing influence of the neighbours, whereas simple superposition of the isolated monomer deformation densities may lead to an apparent decrease due to the overlap with the negative contours of the neighbouring atom. Depending on which of these factors is the dominant one, an increase or decrease in the lone-pair density may be observed.

These facts will be illustrated by recent results on some hydrates of nickel salts. The charge densities have been determined at RT and 25K by multipole refinement against single-crystal X-ray intensity data. The charge densities based on the fitted deformation functions of all atoms in the structure are compared with the individual densities calculated from deformation functions of only Ni or the separate water molecules. In this way the effect of simple superposition of the individual densities has been studied. Polarization of the lone-pair densities, reflecting the different coordination of the water molecules, is clearly evident, an effect which is normally considered too small to be detected experimentally.

The spin densities have been determined by polarized neutron diffraction at 1.5 K in a magnetic field of 4.6 T. The charge and spin densities observed are in good agreement with those expected from ligand field theory for a d^8 electron configuration of Ni^{2+} in both weak and strong ligand fields.